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Note

Optical ligand-to-ligand charge transfer of (1,2-diimine)Pt(II)- $(\mu$ -S₂MS₂) with M = Mo(VI) and W(VI)⁻¹

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Abstract

The binuclear complexes $Pt^{II}(1,2-dimine)(\mu-S_2M^{VI}S_2)$ with 1,2-dimine = 2,2'-bipyridyl and biacetyl bis(anil) and M = Mo and W show long-wavelength absorption bands above 550 nm which are assigned to ligand-to-ligand charge transfer transitions from the bridging sulfide to the dimine ligands. © 1997 Elsevier Science S.A.

Keywords: Charge transfer; Platinum complexes; Diimine complexes; Tetrathiometallate complexes

1. Introduction

Coordination compounds which contain reducing and oxidizing ligands are frequently characterized by long-wavelength ligand-to-ligand charge transfer (LLCT) absorptions in their electronic spectra [1,2]. This type of optical charge transfer has attracted much attention in recent years. Appropriate acceptor ligands are porphyrins and 1,2-diimines including 2,2'-bipyridyl while anions such as carbanions and thiolates were employed as donor ligands. Organic monoand di-thiolates constitute the largest group of suitable donors for LLCT. In this context it is quite surprising that inorganic thiolates have not been utilized for such studies. We explored this possibility and selected MoS_4^{2-} and WS_4^{2-} as candidates for this purpose. Tetrathiometallates are well known to coordinate as bidentate ligands via two sulfur atoms. A large number of transition metal complexes with these ligands [3] including $[Pt^{II}(\mu-S_2M^{VI}S_2)_2]^{2-}$ (M=Mo and W) have been described [4.5]. We were confident to identify LLCT absorptions in the electronic spectra of the binuclear compounds Pt^{II}(1,2-diimine)(μ -S₂M^{VI}S₂) since numerous complexes of the type Pt^{II}(1,2-diimine) (organic dithiolate) have been shown to display characteristic long-wavelength LLCT bands [6-10]. Since a variety of such complexes with organic dithiolates as ligands have been already prepared [6,7,9,11], the synthesis of our target compounds Pt^{II}(1,2-diimine)-

 $(\mu$ -S₂M^{VI}S₂) was anticipated to be not too difficult. As 1,2dimines we chose bipy = 2,2'-bipyridyl and baba = biacetyl bis(anil).

2. Experimental

2.1. Materials

Pt(bipy)Cl₂, Pt(CH₃CN)₂Cl₂, $(NH_4)_2MoS_4$ and $(NH_4)_2$ -WS₄ were commercially available by Aldrich. $(Bu_4N)_2MoS_4$ [12], $(Bu_4N)_2WS_4$ [12] and baba [13] were prepared according to published procedures. The purity of all substances was confirmed by UV–Vis spectroscopy and elemental analysis. All solvents were spectrograde.

2.2. Syntheses

2.2.1. $Pt(bipy)(\mu - S_2 MoS_2)$

A suspension of 422 mg (10^{-3} mol) Pt(bipy)Cl₂ and 0.5 g bipy in 200 ml water was heated to 85°C under stirring until a solution which contained [Pt(bipy)₂]Cl₂ was obtained. To this solution which was filtered, saturated with argon, and heated to 60°C was slowly added 260 mg (10^{-3} mol) (NH₄)₂MoS₄ in 20 ml water. A dark-red product precipitated within minutes. Stirring was continued for 15 min. The product was collected by filtration, washed with water, methanol,

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¹ Dedicated to Professor Waldemar Adam on the occasion of his 60th birthday.

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 CS_2 and ether, and dried under reduced pressure. The dry material was suspended in 50 ml CH_2Cl_2 . This suspension was saturated with argon and stirred for 20 h in order to extract an excess of bipy. The solid was collected by filtration, washed with ether, and dried under vacuum. Yield: 0.2 g (35%). In order to remove further traces of soluble impurities the product was extracted with CH_2Cl_2 in a Soxhlet apparatus for 30 h. The analytically pure, dark-red powder was collected by filtration, washed with CS_2 and ether, and dried under vacuum. *Anal.* Calc. for $C_{10}H_8N_2S_4MoPt$: C, 20.87; H, 1.40; N, 4.87. Found: C, 20.43; H, 1.42; N, 4.77%.

2.2.2. $Pt(bipy)(\mu - S_2WS_2)$

To an argon-saturated solution of 797 mg (10^{-3} mol) $(Bu_4N)_2WS_4$ in 50 ml CH₂Cl₂ was added 422 mg (10^{-3} mol) Pt(bipy)Cl₂. This mixture was heated under reflux for 60 h. The dark-red precipitate was collected by filtration, washed with CH₂Cl₂ and ether, and dried under vacuum. Yield: 0.25 g (38%). For removing further trace impurities the procedure as described above was used. *Anal.* Calc. for C₁₀H₈N₂S₄WPt: C, 18.10; H, 1.21; N, 4.22. Found: C, 18.05; H, 1.28; N, 4.21%.

2.2.3. $Pt(baba)(\mu - S_2 MoS_2)$

To a filtered solution of 348 mg (10^{-3} mol) Pt(CH₃CN)₂-Cl₂ in 25 ml of argon-saturated 1,2-dichloroethane was added a solution of 473 mg $(2 \times 10^{-3} \text{ mol})$ baba in 25 ml of argonsaturated 1,2-dichloroethane. The resulting solution was heated to reflux for 20 min. A dark-brown coloration indicated the formation of [Pt(baba)₂]Cl₂. To the filtered solution was added 709 mg (10^{-3} mol) (Bu₄N)₂MoS₄ in small portions. The color of the solution changed to dark-red. A dark-blue product precipitated. The reaction mixture was stirred for 10 h at r.t. The precipitate was collected by filtration, washed with CH₂Cl₂ and ether, and dried under reduced pressure. Yield: 0.28 g (43%). A further purification was achieved by Soxhlet extraction as described above. *Anal*. Calc. for C₁₆H₁₆N₂S₄MoPt: C, 29.31; H, 2.46; N, 4.27. Found: C, 28.75; H, 2.80; N, 4.42%.

2.2.4. $Pt(baba)(\mu - S_2WS_2)$

The synthesis was carried out in analogy to the preparation of the corresponding molybdenum complex. $(Bu_4N)_2MoS_4$ was replaced by 797 mg (10^{-3} mol) $(Bu_4N)_2WS_4$. The reaction mixture was stirred for 12 h at 60°C. The product was isolated as dark-blue powder. Yield: 0.19 g (26%). Anal. Calc. for C₁₆H₁₆N₂S₄WPt: C, 25.85; H, 2.17; N, 3.77. Found: C, 25.12; H, 1.96; N, 3.89%.

2.3. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or an Uvikon 860 absorption spectrometer.

3. Results

The four compounds $Pt(1,2-diimine)(\mu-S_2MS_2)$ with 1,2-diimine = bipy and baba and M = Mo and W are synthesized according to the equations

$$[Pt(diimine)_2]Cl_2 + (NR_4)_2MS_4$$

$$\rightarrow Pt(diimine)(\mu - S_2MS_2) + diimine + 2NR_4Cl_2$$

or

 $Pt(diimine)Cl_2 + (NR_4)_2MS_4$

 \rightarrow Pt(diimine)(μ -S₂MS₂) + 2NR₄Cl

The analytically pure complexes are obtained as dark-red (diimine = bipy) to dark-blue (baba) powders. While the compounds $Pt(bipy)(\mu-S_2MS_2)$ are completely insoluble in all common solvents (in DMF and DMSO both complexes are decomposed), $Pt(baba)(\mu-S_2MS_2)$ show a residual solubility in various organic solvents.

The electronic spectra of solid Pt(diimine) (μ -S₂MS₂) are recorded as scattered-transmission spectra (Fig. 1 and Table 1). In addition, the complexes Pt(baba) (μ -S₂MS₂) are sufficiently soluble to measure the absorption spectra in solution. These spectra are very similar to the solid state spectra. However, the longest-wavelength absorption undergoes a solvent-dependent shift. For example, Pt(baba) (μ -S₂WS₂) displays this band at $\lambda_{max} = 635$ nm in the solid state and in CHCl₃ while it is shifted to 585 nm in acetone (Fig. 2). Such a negative solvatochromism has also been observed for other complexes of the type Pt(1,2-diimine)(dithiolate) [6,7,9]. The complexes Pt(1,2-diimine)(μ -S₂MS₂) are not luminescent up to 900 nm.



Fig. 1. Scattered-transmission spectrum of a suspension of finely powdered $Pt^{II}(bipy)(\mu-S_2Mo^{VI}S_2)$ in n-hexane at room temperature, 1 cm cell.

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Scattered-transmission maxima of powdered $Pt(1,2\text{-diimine})\,(\,\mu\text{-}S_2MS_2)$ in n-hexane; λ_{max} (nm)

$Pt(bipy)(\mu - S_2MoS_2)$	240	282	314	360	440	570	
$Pt(bipy)(\mu - S_2WS_2)$	220	284	315		410	580	
$Pt(baba)(\mu - S_2MoS_2)$	245	274	320	375	420		640
$Pt(baba)(\mu - S_2WS_2)$	244	292		368	420		635



Fig. 2. Electronic absorption spectrum of $[Pt^{II}(baba)(\mu-S_2W^{VI}S_2)]$ at room temperature in (a) acetone (---) and (b) trichloromethane (_____), 5 cm cell.

4. Discussion

Several procedures can be applied to the synthesis of complexes of the type $Pt^{II}(1,2-diimine)(dithiolate)$ [6,7,9,11]. If these compounds are soluble in the solvent which is used for the preparation the reaction between $Pt(dimine)Cl_2$ and an alkali or tetraalkyl ammonium salt of the dithiolate will yield a solution of the desired complex. From these solutions the compounds can be isolated by evaporation of the solvent or precipitation by another solvent. However, this procedure is not always successful if the Pt(diimine)(dithiolate) is insoluble. Since the solubility of $Pt(diimine)Cl_2$ is also rather small it may occur as an impurity of the product Pt(diimine)(dithiolate). In this case it is preferable to generate first $[Pt(diimine)_2]^{2+}$ which is soluble in polar solvents. Although its reaction with the dithiolate may lead to the precipitation of mixtures which contain Pt(diimine)-(dithiolate) and the salt $[Pt(diimine)_2]$ (dithiolate), the salt can be converted to the desired mixed-ligand complex by extraction of excess diimine with suitable solvents. Since the complexes Pt(1,2-diimine) (μ -S₂MS₂) with diimine = bipy and baba and M = Mo and W are rather insoluble their preparation was achieved according to these considerations.

In analogy to other complexes of the type Pt(1,2-diimine)-(dithiolate) the conspicuous long-wavelength absorptions of $Pt(1,2-diimine)(\mu-S_2MS_2)$ which largely determine the colors of these compounds are assigned to LLCT transitions [1,2,6–10]. They should involve the promotion of electrons from the bridging sulfide ligands to π^* orbitals of the diimine ligands. The LLCT assignment is supported by several other observations. For example, the compounds Pt(1,2-diimine)- $(\mu$ -S₂MS₂) can be viewed as being composed of the homoleptic complexes $[Pt(1,2-diimine)_2]^{2+}$ and $[Pt(\mu-S_2 MS_2$)₂]²⁻. These ions do not show absorptions above 550 nm [4,5,14–16]. Accordingly, the bands of the mixed-ligand complexes which appear at $\lambda > 550$ nm should result from the interaction of the diimine and MS₄²⁻ ligands and hence are logically assigned to $MS_4^{2-} \rightarrow diamine LLCT$ transitions. The donor atoms are assumed to be the sulfide ligands which act also as donors for the ligand-to-metal charge transfer

(LMCT) transitions of the isolated MS_4^{2-} anions ($\lambda_{max} =$ 468 nm for M = Mo and 392 nm for W) [3,12]. The LLCT absorptions of $Pt(baba)(\mu-S_2MS_2)$ appear at longer wavelength than those of the corresponding bipy complexes (Table 1). This result is in accord with the larger acceptor strength of baba compared to that of bipy [17]. Finally, the dependence of the transition energies of the longest-wavelength bands of Pt(baba) (μ -S₂MS₂) on the solvent polarity (Fig. 2) is also consistent with an LLCT assignment [1,2]. fig The tetrathiometallates of d^o metals can not only function as electron donors but also as acceptors owing to their oxidizing metal centers. In this context it is quite intriguing that coordination of MS_4^{n-} anions to reducing metals such as Re(I) [18] or Cu(I) [19] leads to the appearance of metal-to-metal charge transfer (MMCT) absorptions in the electronic spectra of the corresponding polynuclear complexes.

Acknowledgements

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